



Thermodynamics of hydrolysis of cellulose to glucose from 0 to 100 °C: Cellulosic biofuel applications and climate change implications



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ABSTRACT

Hydrolysis of cellulose to glucose is a key reaction in renewable energy from biomass and in mineralization of soil organic matter to CO₂. Conditional thermodynamic parameters, $\Delta_{\text{hyd}}G'$, $\Delta_{\text{hyd}}H'$, and $\Delta_{\text{hyd}}S'$, and equilibrium glucose concentrations are reported for the reaction $C_6H_{10}O_5(\text{cellulose}) + H_2O(l) \rightleftharpoons C_6H_{12}O_6(aq)$ as functions of temperature from 0 to 100 °C. Activity coefficients of aqueous glucose solution were determined as a function of temperature. The reaction free energy $\Delta_{\text{hyd}}G'$ becomes more negative as temperature increases, suggesting that producing cellulosic biofuels at higher temperatures will result in higher conversion. Also, cellulose is a major source of carbon in soil and is degraded by soil microorganisms into CO₂ and H₂O. Therefore, global warming will make this reaction more rapid, leading to more CO₂ and accelerated global warming by a positive feedback.

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1. Introduction

Most of the carbon fixed by terrestrial plants is used to synthesize lignocellulose. As one of the largest reservoirs of organic compounds on the planet, lignocellulose has the potential to replace a significant amount of petroleum as a feedstock for production of chemicals and liquid fuels. Because lignocellulose is a major part of soil organic matter, oxidation of lignocellulose to CO₂ is a major contributor of atmospheric CO₂, but the temperature dependence of the rate of this reaction is very uncertain.

Lignocellulose consists of approximately equal parts lignin, cellulose and hemicellulose. Lignin is a two-dimensional polyphenol, cellulose is a largely crystalline polymer of glucose with a coiled structure, and hemicellulose consists of relatively short polysaccharides of various sugars with no long range structural order. Hemicellulose is relatively easily separated and solubilized by hydrolysis with acid or base catalysis under mild conditions and is readily metabolized to CO₂ by soil organisms. The difficulty of depolymerizing and solubilizing the lignin and cellulose in lignocellulose is a major roadblock to use of biomass as a chemical feedstock and may limit the rate of oxidation to CO₂ in soil. The hydrolysis reactions of lignin and cellulose may be significant in turnover of soil organic matter with potential positive feedback exacerbating global warming, but it is unknown whether these

reactions occur to a significant extent at normal soil temperatures. The potential use of lignocellulose as a feedstock for chemical and fuel production also depends on the thermodynamics of the depolymerizing hydrolysis reactions.

Several exozymes that catalyze hydrolysis of lignocellulose are known [1], but whether or not these could be used in an economically viable process depends on the extent of reaction that can be obtained. Therefore, it is important to quantify the thermodynamics of hydrolysis of lignocellulose. This study quantifies the thermodynamics of the cellulose component of lignocellulose to aqueous glucose as a function of temperature from 0 to 100 °C.

2. Thermodynamic data

Goldberg et al. [2] reports $\Delta_{\text{cr}}H^\circ$, $\Delta_{\text{cr}}S^\circ$, $\Delta_{\text{cr}}G^\circ$, and $\Delta_{\text{cr}}C_p^\circ$ for the hydrolysis of four cellulose allomorphs (amorphous cellulose, cellulose I, cellulose II and cellulose III) to crystalline anhydrous α -D-glucose at 25 °C (Table 1) and heat capacities for the allomorphs from 2 to 300 K. The calculation assumes the molar entropy of cellulose per monomer unit is equal to the entropy change of heating cellulose from absolute zero to room temperature, residual entropy was neglected, since it could not be determined. Boerio-Goates [3] reports heat capacity data for crystalline anhydrous α -D-glucose from 10 to 340 K. Osborne et al. [4] reports heat capacity data on liquid water from 273 to 373 K.

Many references report glucose solubility in water [5–9], but due to difficulties of making measurements on saturated glucose

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Table 1

$\Delta_{cr}H_{ref}^\circ$, $\Delta_{cr}S_{ref}^\circ$ and $\Delta_{cr}C_p^\circ$ values for Eqs. (5) and (6) were taken from reference 2. Heat capacity coefficients, q_i , were obtained by fitting Eq. (9) to extrapolated heat capacity values, see text around Eq. (8).

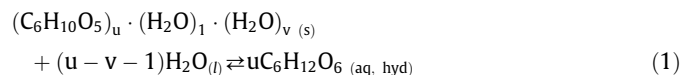
	Amorphous cellulose	Cellulose I	Cellulose II	Cellulose III
$\Delta_{cr}H_{ref}^\circ$ (kJ/mol)	$-(6.4 \pm 2.7)$	8.2 ± 3.7	13.6 ± 3.3	9.9 ± 4.1
$\Delta_{cr}S_{ref}^\circ$ (J/mol K)	$-(28.6 \pm 3.3)$	$-(24 \pm 11)$	$-(5 \pm 16)$	$-(0.6 \pm 19)$
$\Delta_{cr}C_p^\circ$ (J/mol K)	$-(47.3 \pm 3.0)$	$-(37 \pm 11)$	$-(22 \pm 15)$	$-(18 \pm 17)$
q_0 (J mol ⁻¹ K ⁻¹)	93.3460	-76.5740	-117.0000	-126.7400
q_1 (J mol ⁻¹ K ⁻²)	-1.0488	0.4127	0.8477	0.9178
q_2 (J mol ⁻¹ K ⁻³)	0.0026	-0.0009	-0.0018	-0.0018
q_3 (J mol ⁻¹ K ⁻⁴)	$-2 \cdot 10^{-6}$	0	0	0

solutions, the results differ significantly. Some reports [7,8] give solubility as mass of glucose per liter of solution, but reliable solution density data to convert these to temperature independent, and thus thermodynamically useful molal units, are not available. Because reliable density data over the range of temperatures analyzed in this study are not available, only references that give solubility in mass fractions were used. Examination of experimental procedures indicates the data published by Young [6] are the most reliable and cover sufficient temperature range for this study, Table 2.

Vapor pressure measurements of aqueous glucose solutions was reported by Taylor and Rowlinson [10]. These data were used to calculate activity coefficients of aqueous glucose.

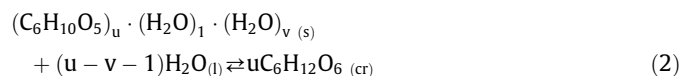
2.1. Reactions

The reaction of interest is cellulose hydrolysis in water to produce an aqueous solution of glucose,

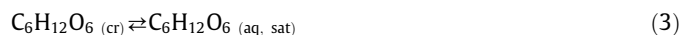


$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_v(s)$ is cellulose, u is the average number of monosaccharide units in the polymer, v is the average number of waters of hydration [2], $C_6H_{12}O_6(aq, hyd)$ is glucose in the cellulose hydrolysis equilibrium solution. No direct thermodynamic measurements have been made on this reaction, and

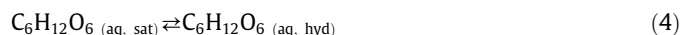
therefore, the reaction was divided into two reactions for which thermodynamic data are available. One reaction is hydrolysis of cellulose to crystalline glucose,



where $C_6H_{12}O_6(cr)$ is anhydrous α -D-glucose. Even though α -D-glucose monohydrate $C_6H_{12}O_6 \cdot H_2O$ is the most thermodynamically stable form up to 50 °C, reaction (2) was used in the entire temperature region where thermodynamic values were estimated. The product of reaction (1) is anhydrous α -D-glucose and the reactant in reaction (3) is anhydrous α -D-glucose. Therefore, even though it is not the most thermodynamically stable form below 50 °C, anhydrous α -D-glucose is used to complete the Hess' law cycle in Scheme 1. The other reaction is dissolution of crystalline glucose to make the final aqueous solution.



where $C_6H_{12}O_6(aq, sat)$ is glucose in a saturated aqueous solution. Completing the cycle also requires correction for the thermodynamics of dilution of glucose since the equilibrium concentrations differ, i.e. saturated and in equilibrium with cellulose.

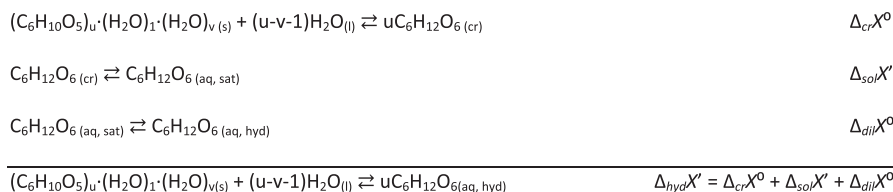


Scheme 1 shows how the thermodynamic data for reactions (2), 3 and 4 are combined to determine the thermodynamics of reaction (1).

Table 2

Solubility of anhydrous α -D-glucose(cr) in water obtained from w values in Table 1 in reference 6. Molality is denoted b and mass fraction is denoted w . Conversion between b and w is done with the equation $b = w/[180.16(1-w)]$, where 180.16 is the molar mass of glucose. Conditional equilibrium constants (K'_{sol}) and conditional Gibbs energy changes ($\Delta_{sol}G'$) were calculated from solubilities for dissolution of anhydrous α -D-glucose in water.

θ (°C)	w (wt%)	T (K)	b (mol/kg H ₂ O) = K'_{sol}	$\Delta_{sol}G'$ (kJ/mol)
-12.06	49.81	261.09	5.509	-3.7042
-10.00	50.49	263.15	5.660	-3.7924
0.00	53.80	273.15	6.464	-4.2381
10.00	57.19	283.15	7.414	-4.7162
20.00	60.65	293.15	8.554	-5.2313
30.00	64.18	303.15	9.945	-5.7895
40.00	67.78	313.15	11.679	-6.3989
50.00	71.46	323.15	13.900	-7.0710
54.71	73.22	327.86	15.177	-7.4136



Scheme 1. Separating the cellulose hydrolysis to aqueous glucose reaction into components.

2.2. Cellulose hydrolysis to solid glucose

The thermodynamics of reaction (2) can be extrapolated from 25 to 100 °C by assuming $\Delta_{cr}C_p^\circ$ does not change with temperature and using the value of $\Delta_{cr}C_p^\circ$ (Table 1) from Goldberg et al. [2] as a constant in integrating $dH = \int C_p dT$ and $dS = \int (C_p/T) dT$, i.e.,

$$\Delta_{cr}H^\circ = \Delta_{cr}H_{ref}^\circ + \Delta_{cr}C_p \circ (T - T_{ref}) \quad (5)$$

$$\Delta_{cr}S_{ref}^\circ = \Delta_{cr}S_{ref}^\circ + \Delta_{cr}C_p \hat{A}^\circ \ln(T/T_{ref}) \quad (6)$$

$\Delta_{cr}H_{ref}^\circ$ and $\Delta_{cr}S_{ref}^\circ$ are the standard reaction enthalpy and entropy at the reference temperature 25 °C, taken from Goldberg et al. [2] (Table 1).

The standard Gibbs energy change of reaction (2), $\Delta_{cr}G^\circ$, was then calculated with the equation

$$\Delta_{cr}G_{ref}^\circ = \Delta_{cr}H_{ref}^\circ - T\Delta_{cr}S_{ref}^\circ \quad (7)$$

To test whether assuming constant $\Delta_{cr}C_p^\circ$ leads to a significant error in the final results, the heat capacity data for cellulose [2] and anhydrous α -D-glucose [3] were fit to

$$C_p(T) = p_1 D(\Theta_D) + p_2 D(\Theta_E) + p_3 T + p_4 T^2 \quad (8)$$

and extrapolated to 100 °C. $C_p(T)$ is the heat capacity as a function of temperature, $D(\Theta_D)$ is the Debye function, Θ_D is the Debye temperature, $E(\Theta_E)$ is the Einstein function, Θ_E is the Einstein temperature, T is Kelvin temperature, and p_1 , p_2 , p_3 and p_4 are coefficients that satisfy $p_1 + p_2 + p_3 + p_4 = 1$. The fitted parameters are given in Table 3. The data were then corrected for cellulose water content and crystallinity and averaged as described by Goldberg et al. [2]. The extrapolated C_p data were then used to find $\Delta_{cr}C_p^\circ$, which was then used to extrapolate the $\Delta_{cr}G^\circ$, $\Delta_{cr}H^\circ$, and $\Delta_{cr}S^\circ$ of reaction (2) up to 100 °C. Because the results did not differ significantly from the approximation of constant $\Delta_{cr}C_p^\circ$, Eqs. (5) and (6) are used in all subsequent calculations.

Using the extrapolated heat capacities of cellulose and anhydrous α -D-glucose and the water heat capacity determined by Osborne et al. [4], the heat capacity change, $\Delta_{cr}C_p^\circ$, for reaction (2) was determined for each of the cellulose allomorphs and fit to a third order polynomial in T where T is temperature in Kelvins.

$$\Delta_{cr}C_p(T) = q_0 + q_1 T + q_2 T^2 + q_3 T^3 \quad (9)$$

The values of q_0 , q_1 , q_2 , and q_3 are given in Table 1.

$\Delta_{cr}C_p(T)$ for reaction (2) was extrapolated to 100 °C and substituted into the equations $dH = \int C_p dT$ and $dS = \int (C_p/T) dT$, which were then integrated from 25 °C to 100 °C.

$$\Delta_{cr}H_{ref}^\circ = \Delta_{cr}H_{ref}^\circ + \frac{1}{4} q_3 (T^4 - T_{ref}^4) + \frac{1}{3} q_2 (T^3 - T_{ref}^3) + \frac{1}{2} q_1 (T^2 - T_{ref}^2) + q_0 (T - T_{ref}) \quad (10)$$

$$\Delta_{cr}S_{ref}^\circ = \Delta_{cr}S_{ref}^\circ + \frac{1}{3} q_3 (T^3 - T_{ref}^3) + \frac{1}{2} q_2 (T^2 - T_{ref}^2) + q_1 (T - T_{ref}) + q_0 \ln\left(\frac{T}{T_{ref}}\right) \quad (11)$$

Substituting Eqs. (10) and (11) into (7), and comparing $\Delta_{cr}G^\circ$ values found from $\Delta_{cr}C_p^\circ$ described by Eq. (8) and found from constant $\Delta_{cr}C_p^\circ$, indicates the approximation in the latter method causes an average error of 0.16% and a maximum error of 1.12% compared with Eq. (8), thus justifying the use of Eqs. (5) and (6) in subsequent derivations.

2.3. Glucose solution

The thermodynamic parameters for reaction (3), solution of crystalline glucose into water, are based on the solubility of anhydrous α -D-glucose in water, Table 2. For practical purposes, concentrations are more convenient than activities, so conditional thermodynamic parameters of dissolution of glucose in water based on molality were determined. The conditional equilibrium constant for reaction (3) is

$$K'_{sol} = b_{sol}^{eq} \quad (12)$$

where b_{sol}^{eq} is the equilibrium solubility of glucose expressed in molal units. The conditional equilibrium constants of reaction (3) are given in Table 2. (Note that a prime symbol refers to a saturated glucose solution as a specified condition.)

The conditional enthalpy of dissolution of glucose in water, $\Delta_{sol}H'$, is determined with the van't Hoff relation

$$-\frac{\Delta_{sol}H'}{R} = \frac{d \ln K'_{sol}}{d(1/T)} \quad (13)$$

The van't Hoff plot is shown in Fig. 1 with data from Table 2 fitted to a second order polynomial in T^{-1} .

$$\ln K'_{sol} = mT^{-2} + nT^{-1} + k \quad (14)$$

m , n and k are constants given in Table 4. The first derivative of the polynomial gives the enthalpy change for dissolution as

$$\Delta_{sol}H' = -R(2mT^{-1} + n) \quad (15)$$

Values of $\Delta_{sol}H'$ are given in Table 5.

The conditional Gibbs energy change for dissolution of glucose in water, $\Delta_{sol}G'$, is related to the conditional equilibrium constant by

$$\Delta_{sol}G' = -RT \ln K'_{sol} \quad (16)$$

The values of $\Delta_{sol}G'$ given in Table 4 were then fitted to the function,

$$\Delta_{sol}G' = \Delta H_l - \Delta a T \ln(T) - \frac{1}{2} \Delta b T^2 - \frac{1}{2} \Delta c T^{-1} + IT \quad (17)$$

Table 3

Coefficients for Eq. (8) obtained by fitting heat capacity data for cellulose from reference 2 and for anhydrous α -D-glucose(cr) from reference 3.

	p_1	Θ_D (K)	p_2	Θ_E (K)	p_3	p_4	%RMS
Cel. Am. 24 h	0.0241	285.10	0.0505	921.95	$2.716 \cdot 10^{-6}$	0	1.577999
Cel. Am. 30 h	0.0245	287.40	0.0520	938.33	$2.709 \cdot 10^{-6}$	0	1.732902
Cel. Am. 36 h	0.0213	272.21	0.0310	854.85	$5.297 \cdot 10^{-6}$	0	1.183929
Cel. I β	0.0202	265.84	0.0224	797.81	$6.082 \cdot 10^{-6}$	0	0.924771
Cel. II 25 °C	0.0186	258.12	0.0154	735.23	$7.757 \cdot 10^{-6}$	0	0.90598
Cel. II 70 °C	0.0194	263.13	0.0222	788.12	$6.099 \cdot 10^{-6}$	0	1.036268
Cel. II 145 °C	0.0198	266.77	0.0251	821.86	$5.667 \cdot 10^{-6}$	0	1.138173
Cel. III -33 °C	0.0194	263.64	0.0225	785.44	$5.955 \cdot 10^{-6}$	0	1.068027
Cel. III 25 °C	0.0185	256.85	0.0160	720.36	$7.321 \cdot 10^{-6}$	0	0.839996
Cel. III 130 °C	0.0200	267.58	0.0255	817.55	$5.782 \cdot 10^{-6}$	0	1.122759
α -D-glucose(cr)	0.8582	328.92	2.5036	1795.93	0	0.6486	0.158449

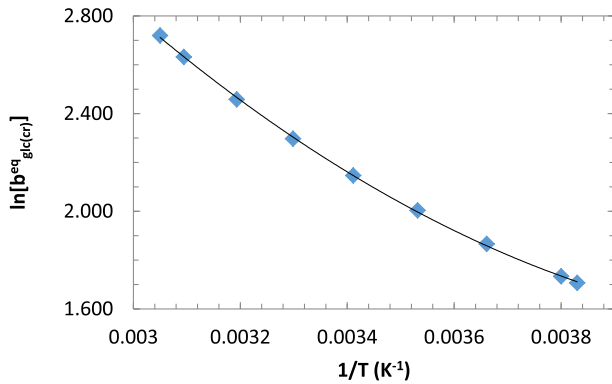


Fig. 1. Van't Hoff plot for dissolution of crystalline α -D-glucose in water, $C_6H_{12}O_6(cr) \rightleftharpoons C_6H_{12}O_6(aq)$. The line going through the points is a second order polynomial fit.

Table 4

Parameters for Eqs. (14) and (17) obtained by fitting K'_{sol} and $\Delta_{sol}G'$ values in Table 2. Parameters, $\alpha_{i,j}$, for the Margules Eq. (23) were obtained from vapor pressure data in reference 10 as explained in the text around Eqs. (22) and (23).

m (J/mol K ²)	675,212
n (J/mol K)	−5927.9
k (J/mol)	14.511
ΔH_1 (J/mol)	1.121324
Δa (J/mol K)	0
Δb (J/mol K ²)	0.251533
Δc (J K/mol)	0.99969
I (J/mol K)	18.83267
$\alpha_{2,0}$	−6.4626
$\alpha_{2,1}$	4.4641
$\alpha_{3,0}$	9.9271
$\alpha_{3,1}$	−9.9685

Table 5

Enthalpy, entropy and Gibbs energy changes for dissolution of anhydrous α -D-glucose (cr) in water extrapolated from 54.71 to 100 °C from Eq. (15), $\Delta_{sol}H'$, Eq. (18), $\Delta_{sol}S'$, and Eq. (17), $\Delta_{sol}G'$. The value of $\Delta_{sol}H'$ at 298.15 found in this research, 11.63 kJ/mol, agrees with the value in a review by Goldberg and Tewari [16], 10.85 kJ/mol. The small difference is probably due to the fact that values reported here are conditional and concentration dependent, while Ref. 16 reports the value at infinite dilution.

T (K)	$\Delta_{sol}H'$ (kJ/mol)	$\Delta_{sol}S'$ (J/mol K)	$\Delta_{sol}G'$ (kJ/mol)
273.15	8.1803	45.4652	−4.2383
278.15	8.9192	48.2123	−4.4908
283.15	9.6320	50.7924	−4.7496
288.15	10.3201	53.2189	−5.0147
293.15	10.9847	55.5040	−5.2861
298.15	11.6270	57.6589	−5.5637
303.15	12.2481	59.6934	−5.8477
308.15	12.8490	61.6170	−6.1379
313.15	13.4308	63.4379	−6.4345
318.15	13.9943	65.1639	−6.7373
323.15	14.5403	66.8020	−7.0464
328.15	15.0697	68.3586	−7.3618
333.15	15.5832	69.8396	−7.6835
338.15	16.0816	71.2505	−8.0114
343.15	16.5654	72.5964	−8.3457
348.15	17.0353	73.8817	−8.6863
353.15	17.4919	75.1107	−9.0331
358.15	17.9357	76.2874	−9.3862
363.15	18.3674	77.4153	−9.7456
368.15	18.7873	78.4979	−10.1113
373.15	19.1959	79.5381	−10.4833

$\Delta_{sol}G'$ is in J/mol, T is in K, and ΔH_1 , Δa , Δb , Δc and I are constants given in Table 4. Function (17) was chosen because it is the most physically meaningful function for fitting free energy

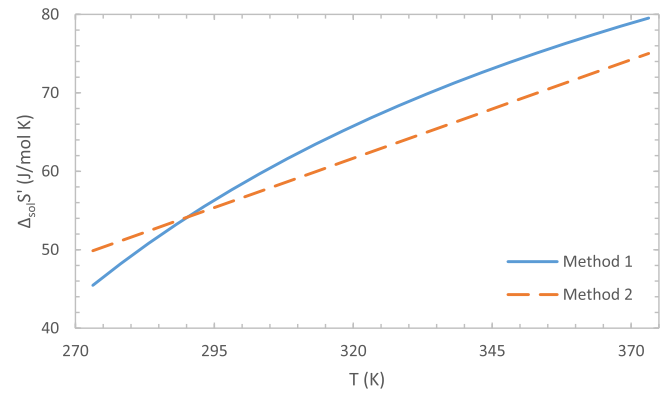


Fig. 2. Comparison of $\Delta_{sol}S'$ found by method 1 - the Gibbs equation (Eq. (18)), and 2 - first derivative of the Gibbs energy (Eq. (19)).

changes as a function of temperature [11]. Eq. (17) was used to extrapolate $\Delta_{sol}G'$ up to 100 °C. The results are given in Table 5.

The conditional entropy of dissolution of glucose in water, $\Delta_{sol}S'$, was calculated in two ways; from the Gibbs equation,

$$\Delta_{sol}S' = (\Delta_{sol}H' - \Delta_{sol}G')/T \quad (18)$$

and by the first derivative of the Gibbs equation with respect to T

$$\Delta_{sol}S' = -\frac{d\Delta_{sol}G'}{dT} \quad (19)$$

The values of $\Delta_{sol}S'$ calculated by the two methods are shown in Fig. 2. The results of the two methods differ on average by 5.66%. The cause of the deviation is probably the loss of significant figures during differentiation in the second method (Eq. (19)). Therefore, since Eq. (18) does not include differentiation, entropy changes calculated from Eq. (18) were selected and presented in Table 5.

2.4. Glucose dilution

The free energy change of reaction (4) $\Delta_{dil}G$, the dilution of aqueous glucose solution from saturated to the concentration in the cellulose hydrolysis mixture, is given as the change in free energy of mixing between the cellulose equilibrium $\Delta_{mix}G_{eq}$ and saturated $\Delta_{mix}G_{sat}$ mixtures

$$\Delta_{dil}G = \Delta_{mix}G_{eq} - \Delta_{mix}G_{sat} \quad (20)$$

The free energy of mixing is a function of composition and temperature and is given by the equation

$$\Delta_{mix}G_{eq} = nRT(x_w \ln x_w + x_{Glc} \ln x_{Glc} + x_w \ln \gamma_w + x_{Glc} \ln \gamma_{Glc}) \quad (21)$$

x_w and x_{Glc} are the mole fractions of water and glucose, respectively; n is the total number of moles in the solution, while γ_w and γ_{Glc} are the activity coefficients of water and glucose, respectively [12].

The activity coefficients were found from vapor pressure measurements done by Taylor and Rowlinson [10], using Raoult's law

$$\gamma_w = \frac{p}{(1 - x_{Glc})p^*} \quad (22)$$

where p is the vapor pressure of the glucose solution of concentration x_{Glc} , and p^* is the vapor pressure of pure water at the same temperature [12,13].

Since the experimental data did not cover the entire range of concentrations and temperatures, it was fitted to the Margules equation and then extrapolated. The Margules equation gives the activity coefficient of the solvent as a function of the solute

concentration and temperature [12,13,15]. It was found that the best fit of the data, with the least number of parameters is given by a two-suffix Margules equation

$$\ln \gamma_w = \alpha_2 x_{Glc}^2 + \alpha_3 x_{Glc}^3 \quad (23a)$$

α_2 and α_3 are temperature-dependent coefficients

$$\alpha_2 = \frac{\alpha_{2,0}}{\theta} + \alpha_{2,1} \quad (23b)$$

$$\alpha_3 = \frac{\alpha_{3,0}}{\theta} + \alpha_{3,1} \quad (23c)$$

where $\theta = T/298.15$ K, while $\alpha_{2,0}$; $\alpha_{2,1}$; $\alpha_{3,0}$; and $\alpha_{3,1}$ are the fitting parameters, given in Table 5. The fitting was done using least-squares regression. The sum of the squares of the residuals was minimized using the GRG-Nonlinear method in Excel Solver, as described by Chapra and Canale [14]. The absolute average deviation of the fit was 11.7%.

The activity coefficient of glucose can be found using the Gibbs-Duhem Eq. [12,13] and is a function of temperature and the mole fraction of water.

$$\ln \gamma_{Glc} = \beta_2 x_w^2 + \beta_3 x_w^3 \quad (24a)$$

β_2 and β_3 are temperature-dependent coefficients, that are related to α_2 and α_3 :

$$\beta_2 = \alpha_2 + \frac{3}{2} \alpha_3 \quad (24b)$$

$$\beta_3 = -\alpha_3 \quad (24c)$$

A review of the theory behind the Margules equation is given by Sandler [15], while Starzak and Mathlouthi [13] give a detailed explanation of how it is applied in practice.

Using Eqs. (20), (21), (23) and (24), $\Delta_{dil}G$ can be determined, knowing the initial and final concentration of the solution $x_{Glc,sat}$ and $x_{Glc,hyd}$, respectively. The initial concentration $x_{Glc,sat}$ is the solubility of glucose in water, which was found using an equation given by Young [6].

$$w_{Glc,sat} = 53.8 + 0.335t + 3.65 \cdot 10^{-4}t^2 \quad (25)$$

where $w_{Glc,sat}$ is the solubility of glucose in water in mass fraction percent and t is temperature in degrees Celsius. The mole fraction of glucose was calculated using the equation

$x_{Glc,sat} = (w_{Glc}/M_{Glc}) / \{(w_{Glc}/M_{Glc}) + [(1 - w_{Glc})/M_w]\}$, where M_{Glc} and M_w are molar masses of glucose and water, respectively. However, there is a problem with the final concentration $x_{Glc,hyd}$: according to Eqs. (20) and (21), $\Delta_{dil}G$ depends on the composition of the hydrolysis mixture, that is, it depends on the equilibrium glucose mole fraction $x_{Glc,hyd}$, related to b_{hyd}^{eq} by the equation $x_{Glc,hyd} = 1 / \{1 + [(M_w / b_{hyd}^{eq})]\}$. On the other hand, according to Eqs. (35) and (36), b_{hyd}^{eq} depends on $\Delta_{dil}G$. So, we have a circular problem, finding b_{hyd}^{eq} requires $\Delta_{dil}G$, while to find $\Delta_{dil}G$ we need b_{hyd}^{eq} . The problem was solved iteratively. Starting from a guess value of $\Delta_{dil}G$, $\Delta_{dil}G$ and b_{hyd}^{eq} were iteratively calculated until convergence was reached. The calculation was done by giving an initial $\Delta_{dil}G$, then calculating b_{hyd}^{eq} and from it a new $\Delta_{dil}G$, until the old and the new values of $\Delta_{dil}G$ became nearly identical, using GRG-Nonlinear method in Excel Solver. The $\Delta_{dil}G$ values determined in this way are given in Table 6.

Enthalpy $\Delta_{dil}H$ and entropy $\Delta_{dil}S$ change of reaction (4) were calculated by fitting a polynomial to $\Delta_{dil}G$ as a function of temperature. The first derivative was used to determine the entropy change: $\Delta_{dil}S = -d(\Delta_{dil}G)/dT$. The enthalpy change was calculated from the Gibbs equation: $\Delta_{dil}H = \Delta_{dil}G + T \Delta_{dil}S$. The values of $\Delta_{dil}H$ and $\Delta_{dil}S$ are given in Table 6. Like with $\Delta_{dil}G$, each cellulose allomorph has its own value, because the equilibrium glucose concentrations differ and thus the dilution thermodynamic parameters are different as well.

2.5. Cellulose hydrolysis to aqueous glucose

The conditional Gibbs energy change for hydrolysis of cellulose to aqueous glucose (reaction (1)), $\Delta_{hyd}G'$, is found by adding the Gibbs energy changes for reactions (2), (3) and (4):

$$\Delta_{hyd}G' = \Delta_{cr}\hat{G}^\circ + \Delta_{sol}G' + \Delta_{dil}G \quad (26)$$

The values of $\Delta_{hyd}H'$, $\Delta_{hyd}S'$ and $\Delta_{hyd}G'$ are given in Table 7. After substituting Eq. (17) for $\Delta_{sol}G'$ and Eqs. (5), (6), and (7) for $\Delta_{cr}\hat{G}^\circ$ and grouping the terms by the power of T , the final result for $\Delta_{hyd}G'$ is

Table 6

Thermodynamic parameters of reaction (4), $C_6H_{12}O_6(aq,sat) \rightleftharpoons C_6H_{12}O_6(aq,hyd)$ obtained as explained in the text following Eq. (25).

T (K)	Amorphous Cellulose			Cellulose 1			Cellulose 2			Cellulose 3		
	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)
273.15	-5.3523	-16.7881	-0.7948	-11.7590	-15.1964	-7.6332	-9.4208	-6.2956	-7.7307	-6.3187	-3.9854	-5.2564
278.15	-5.1303	-15.3996	-0.8516	-11.4586	-13.5853	-7.68043	-8.9911	-4.5407	-7.7331	-5.8602	-2.2101	-5.2474
283.15	-5.0015	-14.4102	-0.9118	-11.2516	-12.3857	-7.73035	-8.6533	-3.2000	-7.7376	-5.4934	-0.8494	-5.2403
288.15	-4.9739	-13.8198	-0.9757	-11.1462	-11.5974	-7.78317	-8.4159	-2.2735	-7.7443	-5.2268	0.0966	-5.2352
293.15	-5.0553	-13.6284	-1.0436	-11.1505	-11.2205	-7.83935	-8.2870	-1.7613	-7.7536	-5.0685	0.6280	-5.2325
298.15	-5.2539	-13.8360	-1.1159	-11.2729	-11.255	-7.89918	-8.2750	-1.6633	-7.7660	-5.0269	0.7449	-5.2328
303.15	-5.5775	-14.4427	-1.1931	-11.5216	-11.7009	-7.96315	-8.3881	-1.9795	-7.7817	-5.1103	0.4471	-5.2364
308.15	-6.0342	-15.4484	-1.2756	-11.9048	-12.5581	-8.03182	-8.6346	-2.7100	-7.8016	-5.3270	-0.2654	-5.2440
313.15	-6.6319	-16.8531	-1.3643	-12.4306	-13.8268	-8.10581	-9.0229	-3.8547	-7.8262	-5.6852	-1.3924	-5.2561
318.15	-7.3786	-18.6569	-1.4597	-13.1074	-15.5068	-8.18598	-9.5612	-5.4137	-7.8563	-6.1933	-2.9340	-5.2738
323.15	-8.2824	-20.8597	-1.5629	-13.9434	-17.5983	-8.27322	-10.2577	-7.3869	-7.8929	-6.8595	-4.8903	-5.2978
328.15	-9.3511	-23.4615	-1.6751	-14.9468	-20.1011	-8.36877	-11.1208	-9.7744	-7.9372	-7.6922	-7.2612	-5.3295
333.15	-10.5928	-26.4624	-1.7976	-16.1258	-23.0153	-8.4741	-12.1588	-12.5761	-7.9907	-8.6996	-10.0467	-5.3704
338.15	-12.0154	-29.8623	-1.9324	-17.4886	-26.3409	-8.59109	-13.3799	-15.7920	-8.0554	-9.8900	-13.2468	-5.4223
343.15	-13.6270	-33.6612	-2.0818	-19.0436	-30.0779	-8.72215	-14.7924	-19.4222	-8.1335	-11.2717	-16.8615	-5.4877
348.15	-15.4354	-37.8591	-2.2488	-20.7988	-34.2263	-8.87049	-16.4046	-23.4666	-8.2284	-12.8531	-20.8908	-5.5698
353.15	-17.4488	-42.4561	-2.4376	-22.7626	-38.7861	-9.0403	-18.2248	-27.9252	-8.3443	-14.6423	-25.3348	-5.6730
358.15	-19.6750	-47.4521	-2.6538	-24.9431	-43.7573	-9.23749	-20.2613	-32.7981	-8.4871	-16.6477	-30.1933	-5.8028
363.15	-22.1220	-52.8471	-2.9054	-27.3487	-49.1398	-9.47036	-22.5224	-38.0853	-8.6650	-18.8776	-35.4665	-5.9678
368.15	-24.7979	-58.6412	-3.2040	-29.9874	-54.9338	-9.75108	-25.0162	-43.7866	-8.8904	-21.3403	-41.1543	-6.1797
373.15	-27.7106	-64.8343	-3.5674	-32.8676	-61.1391	-10.0985	-27.7513	-49.9022	-9.1819	-24.0440	-47.2567	-6.4571

Table 7

Conditional thermodynamic parameters for hydrolysis of cellulose into aqueous glucose – reaction (1), $(C_6H_{10}O_5)_n \cdot (H_2O)_1 \cdot (H_2O)_v(s) + (u-v-1)H_2O(l) \rightleftharpoons uC_6H_{12}O_6(aq, hyd)$, obtained from Eqs. (26), (28), and (29) using data from Tables 4, 5 and 6 with data from Table 1.

T (K)	Amorphous Cellulose			Cellulose 1			Cellulose 2			Cellulose 3		
	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)
273.15	-2.3888	4.2304	-3.5725	5.5471	9.5201	2.9215	12.9102	36.1073	3.0180	12.2123	42.4672	0.5861
278.15	-1.6644	7.5080	-3.7574	6.4013	13.2071	2.7272	13.9689	40.2102	2.7793	13.3197	46.6630	0.3384
283.15	-1.0593	10.2348	-3.9478	7.1361	16.3277	2.5272	14.9094	43.7391	2.5343	14.3093	50.2831	0.0843
288.15	-0.5801	12.4238	-4.1440	7.7446	18.8948	2.3212	15.7249	46.7070	2.2827	15.1740	53.3406	-0.1767
293.15	-0.2335	14.0867	-4.3464	8.2198	20.9204	2.1089	16.4083	49.1259	2.0241	15.9068	55.8476	-0.4448
298.15	-0.0263	15.2339	-4.5555	8.5546	22.4150	1.8897	16.9526	51.0067	1.7581	16.5006	57.8148	-0.7206
303.15	0.0347	15.8752	-4.7718	8.7421	23.3884	1.6632	17.3506	52.3592	1.4842	16.9483	59.2523	-1.0045
308.15	-0.0575	16.0194	-4.9958	8.7749	23.8494	1.4288	17.5950	53.1924	1.2017	17.2426	60.1690	-1.2972
313.15	-0.3100	15.6743	-5.2283	8.6458	23.8062	1.1858	17.6785	53.5146	0.9100	17.3761	60.5733	-1.5993
318.15	-0.7298	14.8473	-5.4702	8.3474	23.2661	0.9332	17.5937	53.3331	0.6082	17.3415	60.4725	-1.9117
323.15	-1.3240	13.5451	-5.7225	7.8725	22.2359	0.6702	17.3332	52.6550	0.2954	17.1313	59.8737	-2.2354
328.15	-2.0998	11.7737	-5.9863	7.2135	20.7216	0.3955	16.8894	51.4864	-0.0297	16.7380	58.7832	-2.5717
333.15	-3.0645	9.5387	-6.2631	6.3630	18.7290	0.1075	16.2550	49.8332	-0.3686	16.1542	57.2066	-2.9220
338.15	-4.2254	6.8452	-6.5550	5.3134	16.2632	-0.1956	15.4222	47.7006	-0.7233	15.3721	55.1494	-3.2884
343.15	-5.5896	3.6979	-6.8642	4.0573	13.3291	-0.5164	14.3835	45.0934	-1.0962	14.3841	52.6164	-3.6732
348.15	-7.1647	0.1012	-7.1939	2.5869	9.9309	-0.8581	13.1311	42.0162	-1.4905	13.1827	49.6121	-4.0797
353.15	-8.9579	-3.9411	-7.5483	0.8948	6.0726	-1.2248	11.6575	38.4730	-1.9105	11.7600	46.1406	-4.5122
358.15	-10.9768	-8.4253	-7.9331	-1.0269	1.7581	-1.6226	9.9549	34.4676	-2.3621	10.1085	42.2058	-4.9764
363.15	-13.2287	-13.3481	-8.3562	-3.1859	-3.0094	-2.0598	8.0154	30.0035	-2.8537	8.2202	37.8111	-5.4807
368.15	-15.7212	-18.7063	-8.8293	-5.5897	-8.2266	-2.5486	5.8314	25.0839	-3.3974	6.0874	32.9598	-6.0371
373.15	-18.4617	-24.4971	-9.3704	-8.2463	-13.8908	-3.1079	3.3951	19.7119	-4.0121	3.7023	27.6549	-6.6641

$$\Delta_{hyd}G' = -\frac{1}{2}\Delta bT^2 + \left\{ \Delta_{cr}C_p\hat{A}^\circ [1 + \ln(T_{ref})] + I - \Delta_{cr}S\hat{A}^\circ_{ref} \right\} T - \frac{1}{2}\Delta cT^{-1} - \left(\Delta_{cr}C_p\hat{A}^\circ + \Delta a \right) T \ln(T) + \left(\Delta_{cr}H\hat{A}^\circ_{ref} + \Delta H_I - \Delta_{cr}C_p\hat{A}^\circ T_{ref} \right) + \Delta_{dil}G \quad (27)$$

Note that in Eqs. (27), (30) and (31) $\Delta_{cr}H^\circ_{ref}$ is in J/mol. Similarly, the conditional enthalpy, $\Delta_{hyd}H'$, and conditional entropy for hydrolysis of cellulose into aqueous glucose, $\Delta_{hyd}S'$, are defined as

$$\Delta_{hyd}H' = \Delta_{cr}H\hat{A}^\circ + \Delta_{sol}H' + \Delta_{dil}H \quad (28)$$

$$\Delta_{hyd}S' = \Delta_{cr}S\hat{A}^\circ + \Delta_{sol}S' + \Delta_{dil}S \quad (29)$$

The dependence of $\Delta_{hyd}H'$ on T is found by substituting Eqs. (5) and (15) into (28). Similarly, the dependence of $\Delta_{hyd}S'$ on T is found by substituting Eqs. (6), (15), (17) and (19) into (29).

$$\Delta_{hyd}H' = \Delta_{cr}C_p\hat{A}^\circ T - 2RmT^{-1} + \left(\Delta_{cr}H\hat{A}^\circ_{ref} - Rn - \Delta_{cr}C_p\hat{A}^\circ T_{ref} + \Delta_{dil}H \right) \quad (30)$$

$$\Delta_{hyd}S' = \frac{1}{2}\Delta bT - (Rn + \Delta H_I)T^{-1} + \left(\frac{1}{2}\Delta c - 2Rm \right) T^{-2} + \left(\Delta_{cr}C_p\hat{A}^\circ + \Delta a \right) \ln(T) + \left[\Delta_{cr}S\hat{A}^\circ_{ref} - I - \Delta_{cr}C_p\hat{A}^\circ \ln(T_{ref}) + \Delta_{dil}S \right] \quad (31)$$

Inserting the values of the constants into Eqs. (26), (30), and (31) gives expressions for the dependence of $\Delta_{hyd}G'$, $\Delta_{hyd}H'$ in J/mol and $\Delta_{hyd}S'$ in J/mol K as functions of T in Kelvins,

The equilibrium concentration of glucose in reaction (1), b_{hyd}^{eq} is calculated from $\Delta_{hyd}G'$ by

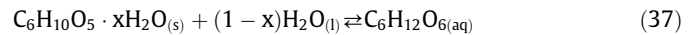
$$\Delta_{hyd}G' = -RT \ln K'_{hyd} \quad (35)$$

$$K'_{hyd} = b_{hyd}^{eq} \quad (36)$$

The values of b_{hyd}^{eq} for the four cellulose allomorphs are given in Table 8. A comparison of b_{hyd} values found with the constant $\Delta_{cr}C_p^\circ$ approximation and with $\Delta_{cr}C_p^\circ$ as a function of temperature, shows

the approximation leads to an average error less than $\approx 0.15\%$, the highest error observed was less than 2.65%.

Mass fraction conversions of cellulose into glucose were calculated from the b_{hyd}^{eq} values. For the hydrolysis reaction per monomer,



$C_6H_{10}O_5$ is the monomer in cellulose, $C_6H_{12}O_6(aq)$ is glucose in aqueous solution, and x is the number of hydration water molecules per glucose monomer. From Goldberg et al. [2], $x = 0.7$. The

Table 8

Equilibrium glucose concentrations from hydrolysis of cellulose to aqueous glucose obtained from Eqs. (35) and (36) with $\Delta_{hyd}G'$ values from Table 7. Estimated uncertainties are given in the footnotes.

T (K)	b_{hyd}^{eq} (mol/kg)			
	Amorphous Cellulose	Cellulose 1	Cellulose 2	Cellulose 3
273.15	4.8216	0.2762	0.2648	0.7725
278.15	5.0774	0.3075	0.3006	0.8639
283.15	5.3494	0.3418	0.3408	0.9648
288.15	5.6395	0.3795	0.3856	1.0765
293.15	5.9497	0.4209	0.4358	1.2002
298.15	6.2825	0.4666	0.4920	1.3374
303.15	6.6410	0.5169	0.5550	1.4897
308.15	7.0286	0.5725	0.6256	1.6592
313.15	7.4497	0.6342	0.7050	1.8483
318.15	7.9095	0.7027	0.7946	2.0601
323.15	8.4144	0.7792	0.8959	2.2980
328.15	8.9727	0.8650	1.0109	2.5667
333.15	9.5948	0.9619	1.1424	2.8719
338.15	10.2944	1.0721	1.2934	3.2209
343.15	11.0896	1.1984	1.4685	3.6238
348.15	12.0055	1.3451	1.6735	4.0937
353.15	13.0773	1.5177	1.9169	4.6497
358.15	14.3564	1.7245	2.2106	5.3188
363.15	15.9212	1.9783	2.5732	6.1428
368.15	17.8973	2.2994	3.0343	7.1879
373.15	20.4998	2.7231	3.6445	8.5683

The uncertainties δb are in the form $b_{hyd}^{eq} \pm \delta b$ and are given as a function of temperature by the following equations.

Amorphous cellulose: $\delta b = 1.279 \cdot 10^{-5} T^3 - 1.146 \cdot 10^{-2} T^2 + 3.454 T - 345.8$.

Cellulose I: $\delta b = 4.697 \cdot 10^{-6} T^3 - 4.197 \cdot 10^{-3} T^2 + 1.261 T - 126.6$.

Cellulose II: $\delta b = 8.456 \cdot 10^{-6} T^3 - 7.553 \cdot 10^{-3} T^2 + 2.265 T - 227.0$.

Cellulose III: $\delta b = 2.302 \cdot 10^{-5} T^3 - 2.056 \cdot 10^{-2} T^2 + 6.170 T - 618.7$.

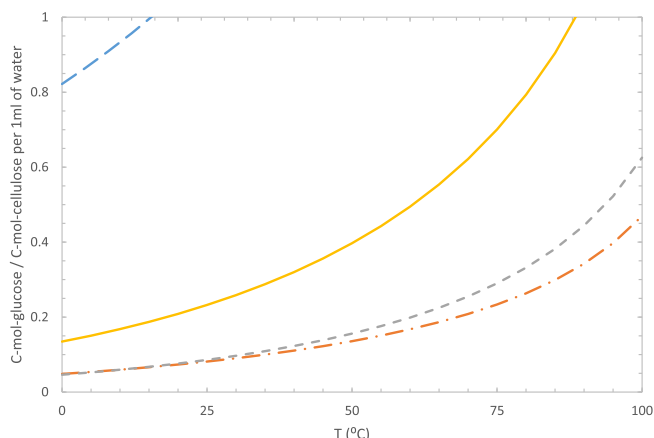


Fig. 3. Mass fraction conversion of cellulose into glucose calculated from Eq. (38), if 1 g of cellulose is mixed with 1 ml of water as the initial reaction mixture. The long-dashed line represents amorphous cellulose (---), the dot-dash line is cellulose I (-.-.-), the short-dashed line is cellulose II (- - -) and the full line is cellulose III.

mass fraction conversion, η , is expressed as the fraction of cellulose carbon converted into glucose: $\eta = n_{glc}/n_{cel,0}$, where n_{glc} is the number of moles of glucose obtained from hydrolysis and $n_{cel,0}$ is number of moles of glucose monomers initially present in the reactor in the form of cellulose. Eq. (38) was used to calculate η .

$$\eta = M_{r,cel} \frac{b_{hyd}^{eq} \rho_w}{1 + (1-x)b_{hyd}^{eq} M_{r,w}} \frac{V_{w,0}}{m_{c,0}} \quad (38)$$

$M_{r,cel}$ is the molar mass of a cellulose monomer including the water of hydration, 174.909 from Goldberg et al. [2], ρ_w is the density of pure water, $M_{r,w}$ is the molar mass of water, $V_{w,0}$ is the initial volume of pure water into which the cellulose was inserted and $m_{c,0}$ is the initial mass of cellulose inserted into the reactor. The denominator accounts for the water of hydration used in the reaction, and $b_{hyd}^{eq} \rho_w V_{w,0}$ is the number of moles of glucose in the solution after hydrolysis. Eq. (38) shows that η depends on the $V_{w,0}$, since if the final glucose solution is diluted below b_{hyd}^{eq} all cellulose will dissolve. Mass fraction conversion values are given in Fig. 3.

3. Discussion

Because the energy cost of obtaining glucose from all forms of cellulose decreases with increasing temperature, global warming may lead to faster mineralization of soil lignocellulose, thus providing a positive feedback increasing the rate of global warming.

Fig. 3 shows that surprisingly large concentrations of glucose can be obtained from hydrolysis of amorphous cellulose and cellulose III. Enzymatic equilibration of amorphous cellulose in water would produce approximately 4.8 molal glucose at room temperature and 20.5 molal glucose in boiling water. Cellulose III equilibrates to approximately 0.7 molal glucose at room temperature and 8.5 molal in boiling water. These two forms of cellulose are thus amenable to use in commercial processes for production of bioethanol or other fuels and chemicals that can be derived from

glucose. Although lower concentrations of glucose are produced at equilibrium, cellulose I and II may also be viable feedstocks for commercial use after treatment, such as ball-milling to reduce the number of hydrogen bonds. The stability of celluloses I, II, and III is due to a high degree of hydrogen bonding. Ball-milling of these forms of cellulose results in amorphous cellulose which is more easily converted into glucose.

Conflicts of interest

There are no conflicts of interest.

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